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Section A.—Mathematical and Physical Sciences.

Bakerian Lecture :—*Rays of Positive Electricity.*

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(Lecture delivered May 22,—MS. received June 4, 1913.)

[Plates 1—3.]

In 1886, Goldstein observed that when the cathode in a vacuum tube was pierced with holes, the electrical discharge did not stop at the cathode; behind the cathode, beams of light could be seen streaming through the holes in the way represented in fig. 1. He ascribed these pencils of light to rays

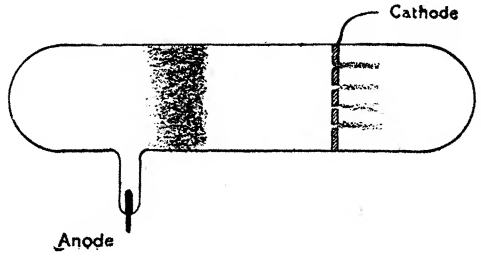

Fig. 1.

passing through the holes into the gas behind the cathode; and from their association with the channels through the cathode he called these rays Kanalstrahlen. The colour of the light behind the cathode depends upon the gas in the tube: with air the light is yellowish, with hydrogen rose colour, with neon the gorgeous neon red, the effects with this gas being exceedingly striking. The rays produce phosphorescence when they strike against the

walls of the tube; they also affect a photographic plate. Goldstein could not detect any deflection when a permanent magnet was held near the rays. In 1898, however, W. Wien, by the use of very powerful magnetic fields, deflected these rays and showed that some of them were positively charged; by measuring the electric and magnetic deflections he proved that the masses of the particles in these rays were comparable with the masses of atoms of hydrogen, and thus were more than a thousand times the mass of a particle in the cathode ray. The composition of these positive rays is much more complex than that of the cathode rays, for whereas the particles in the cathode rays are all of the same kind, there are in the positive rays many different kinds of particles. We can, however, by the following method sort these particles out, determine what kind of particles are present, and the velocities with which they are moving. Suppose that a pencil of these rays is moving parallel to the axis of x, striking a plane at right angles to their path at the point O; if before they reach the plane they are acted on by an electric force parallel to the axis of y, the spot where a particle strikes the plane will be deflected parallel to y through a distance y given by the equation

$$y = \frac{e}{mv^2}\mathrm{A},$$

where e, m, v, are respectively the charge, mass, and velocity of the particle, and A a constant depending upon the strength of the electric field and the length of path of the particle, but quite independent of e, m, or v.

If the particle is acted upon by a magnetic force parallel to the axis of y, it will be deflected parallel to the axis of z, and the deflection in this direction of the spot where the particle strikes the plane will be given by the equation

$$z = \frac{e}{mv}\mathrm{B},$$

where B is a quantity depending on the magnetic field and length of path of the particle, but independent of e, m, v. If the particle is acted on simultaneously by the electric and magnetic forces, the spot where it strikes the plane will, if the undeflected position be taken as origin, have for co-ordinates

$$x = 0, \qquad y = \frac{e}{mv^2}\mathrm{A}, \qquad z = \frac{e}{mv}\mathrm{B}. \tag{1}$$

Thus no two particles will strike the plane in the same place, unless they have the same value of v and also the same value of e/m; we see, too, that if we know the value of y and z, we can, from equation (1), calculate the values of v and e/m, and thus find the velocities and character of the particles composing the positive rays.

From equation (1) we see that

$$z^2 = \frac{e}{m} y \frac{B^2}{A}, \qquad z = y \cdot v \frac{B}{A}. \tag{2}$$

Thus all the particles which have a given value of e/m strike the plane on a parabola, which can be photographed by allowing the particles to fall on a photographic plate. Each type of particle in the positive rays will produce a separate parabola, so that an inspection of the plate shows at a glance how many kinds of particles there are in the rays; the measurement of the parabolas, and the use of equation (2), enables us to find the values of m/e corresponding to them, and thus to make a complete analysis of the gases in the positive rays. To compare the values of m/e corresponding to the different parabolas, we need only measure the values of z on these parabolas corresponding to a constant value of y. We see from equation (2) that the values of e/m are proportional to the squares of the values of z. Thus, if we know the value of e/m for one parabola, we can with very little labour deduce the values of e/m for all the others. As the parabola corresponding to the hydrogen atom is found on practically all the plates, and as this can be at once recognised, since it is always the most deflected parabola, it is a very easy matter to find the values of m/e for the other particles. Photographs made by the positive rays after they have suffered electric and magnetic deflections are reproduced in figs. 2 and 3 (Plate 1). The apparatus I have used for photographing the rays is shown in fig. 4.

A is a large bulb of from 1 to 2 litres capacity in which the discharge passes, C the cathode placed in the neck of the bulb. The position of the front of the cathode in the bulb and the shape of the bulb where it joins the neck D have a very considerable influence on the brightness of the rays and the distribution of velocities among the particles. If the cathode projects into the bulb, the pressure of the gas in the bulb when the rays are the brightest is apt to be inconveniently low, and the same is true when,

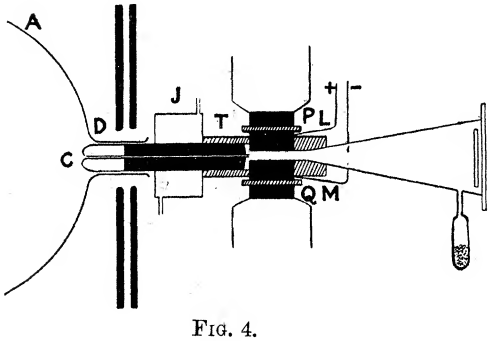

FIG. 4.

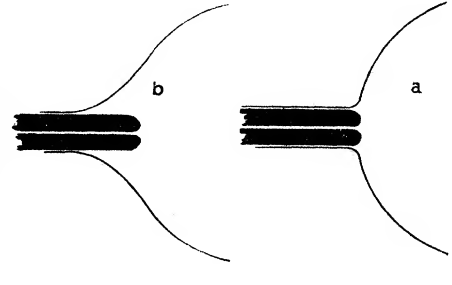

FIG. 5.

though the cathode is kept in the neck, the bulb swells out gradually from the neck instead of starting off abruptly. I have got the best results by making the transition from the neck to the bulb as abrupt as possible and putting the front of the cathode flush with the junction of the neck and the bulb, in the way shown in fig. 5*a*; this gives better results than when the cathode is placed as in fig. 5*b*.

The form of cathode which I have found to give the best pencil of rays is shown in fig. 4. The front of the cathode is an aluminium cap, carefully worked so as to be symmetrical about an axis: this cap fits on to a cylinder made of soft iron with a hole bored along the axis; the object of making the cathode of iron is to screen the rays from magnetic force while they are passing through the hole. A case fitting tightly into this hole contains a long narrow tube which is the channel through which the rays pass into the tube behind the cathode. This tube is the critical part of the apparatus, and failure to obtain a good pencil of rays is generally due to some defect here. As the length of this tube is very long in proportion to its diameter—the length of most of the tubes I have used is about 6 cm. and the diameter from 0·1 to 0·5 mm.—it requires considerable care to get it straight enough to allow an uninterrupted passage to the rays. The method we use is to start with a piece of fine copper tubing and draw it out until the diameter is reduced to the right value, the proper length is cut off, and this is rolled between two surface plates, until optical examination shows that it lets a pencil of light pass without obstruction through the tube; it is useless to attempt to experiment with positive rays unless this tube is exceedingly straight. The rays themselves exert a sand blast kind of action on the tube and disintegrate the metal; after prolonged use the metallic dust may accumulate to such an extent that the tube gets silted up, and obstructs the passage of the rays. The cathode is fixed into the glass vessel by a little wax; the joint is made tight so that the only channel of communication from one side of the cathode to the other is through the tube in the cathode. The wax joint is surrounded by a water jacket J to prevent the wax being heated by the discharge. The arrangements used to produce the electric and magnetic fields to deflect the rays are shown at L and M. An ebonite tube is turned so as to have the shape shown in fig. 4, L and M are two pieces of soft iron with carefully worked plane faces, placed so as to be parallel to each other, these are connected with a battery of storage cells and furnish the electric field. P and Q are the poles of an electromagnet separated from L and M by the thin walls of the ebonite box: when the electromagnet is in action there is a strong magnetic field between L and M; the lines of magnetic force and electric force are by this arrangement parallel to each other and the electric

and magnetic fields are as nearly as possible coterminous. This arrangement was adopted for a special investigation in which it was desirable that the two fields should not overlap; for many purposes, for example, the analysis of the gases in the tube, this condition is not important, and the simpler arrangement shown in fig. 6 answers all the requirements. Here the ebonite box is

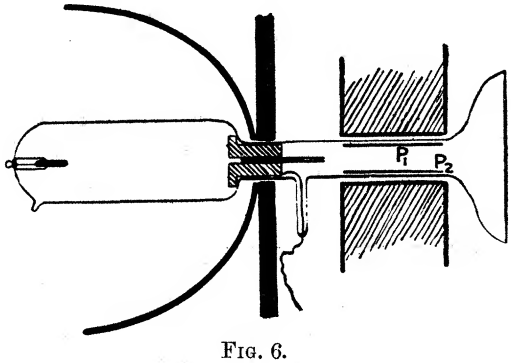

FIG. 6.

done away with, the electric field is produced between two parallel plates of metal, P_1, P_2, and the magnetic field is produced by an electromagnet whose poles are on opposite sides of the tube. The arrangement used for photographing the rays is that designed by Mr. Aston and described in the 'Phil. Mag.,' 1911, vol. 21, p. 227. Plates of soft iron are placed between the electromagnet and the discharge tube to prevent the discharge from being affected by the magnetic field.

The pressure in the tube behind the cathode must be kept very low, this is done by means of a tube containing charcoal cooled by liquid air. The pressure on the other side of the cathode is much higher.

A typical photograph taken with this apparatus is reproduced in fig. 7.

It will be noticed that in addition to the parabolic arcs whose origin has already been discussed, there are a series of lines approximately straight. These secondary lines are due to particles which have been charged for a part only of the time they were in the electric and magnetic fields and are therefore not so much deflected as those which were charged for the whole time and which produce the parabolas. Some particles which are charged when they enter those fields lose their charges before they get through, while others which are uncharged to begin with gain a charge before they leave the fields. We can distinguish between these cases in the following way. Make the magnetic field M (fig. 8) overlap the electric field E, so that in the region EM the particles are exposed to magnetic but not to electric forces.

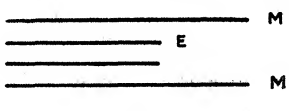

FIG. 8.

A particle which begins by being uncharged and first picks up a charge in this region will experience a magnetic without an electric deflection, so that the trace made on the photograph by the particles which pick up a charge will resemble fig. 9, *a*.

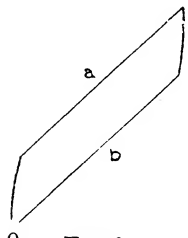

FIG. 9.

Now, consider the trace made by the particles which started with a charge but lost it before they got through: these, when they are in the region EM, will have already experienced a considerable deflection so that the place where they get a magnetic without an electric deflection will be at the most deflected end of the line and the shape of the trace they make on the plate will be somewhat like fig. 9, *b*. An example of this effect is shown in the photograph reproduced in fig. 10.

Unless the pressure in the observation chamber is very low, few of the particles remain charged during the whole of the journey through the electrostatic and magnetic fields, and in this case the parabolas disappear, and only the lines due to the secondaries appear on the plate.

The parabolas are determined by the values of e/m, thus an atom with a single charge would produce the same parabola as a diatomic molecule with a double charge. We can, however, by the following method distinguish between parabolas due to particles with a single charge and those due to particles with more than one charge.

The parabolas are not complete parabolas, but arcs starting at a finite distance from the vertical, this distance is by equation (1) inversely proportional to the maximum kinetic energy possessed by the particle. This maximum kinetic energy is that due to the charge on the particle falling from the potential of the anode to that of the cathode in the discharge tube. Consider now the particles which have two charges: these acquire in the discharge tube twice as much kinetic energy as the particles with a single charge. Some of these doubly charged particles will lose one of their charges while passing through the long narrow tube in the cathode, and will emerge as particles with a single charge; they will, however, possess twice as much kinetic energy as those which have had one charge all the time. Thus the stream of singly charged particles emerging from the tube will consist of two sets, one having twice as much kinetic energy as the other; the particles having twice the kinetic energy will strike the plate nearer to the vertical than the others, and will thus prolong beyond the normal length the arc of the parabola corresponding to the singly charged particle. An example of this is shown in the photograph reproduced in fig. 11, where the line α, due to a singly charged oxygen atom for which $m/e = 16$, is prolonged until its extremity is only half the normal distance from the vertical. The line β on

the photograph gives $m/e = 8$, hence we conclude that this line is due to an atom of oxygen with two charges, whereas if the oxygen line had not been prolonged we should have concluded that β was due to a singly charged atom with an atomic weight 8.

If the atom acquired more than two charges the prolongation of the atomic line would be still longer. If, for example, it could acquire eight charges it would be prolonged until its extremity was only one-eighth of the normal distance from the vertical. An example of this is shown in fig. 12 (Plate 2), where α is the line due to the singly charged mercury atom, this approaches to within one-eighth of the normal distance, and the theory is verified by the appearance on the plate of the lines β, γ, δ, ..., which correspond to mercury atoms with 2, 3, 4, 5, 6, 7 charges. The lines due to the one with 8 charges cannot be detected, but the intensity of the lines diminishes as the charge increases, and it is perhaps legitimate to conclude that with more sensitive apparatus the line corresponding to the atom with eight charges might be detected.

Using this method to distinguish between singly and multiply charged systems we find that the particles which produce the parabolas on the photographic plates may be divided into the following classes :—

1. Positively electrified atoms with one charge.
2. Positively electrified molecules with one charge.
3. Positively electrified atoms with multiple charges.
4. Negatively electrified atoms.
5. Negatively electrified molecules.

The production of a charged molecule involves nothing more than the detachment of a corpuscle from the molecule, that of a charged atom requires the dissociation of the molecule as well as the electrification of the atom. As the results are so different we naturally ask, Is the mechanism by which the charged atoms are produced the same as that which produces the charged molecules? There seems to me to be strong evidence that the charged atoms and molecules are produced by different agents. We not infrequently find that some of the parabolas have characteristic peculiarities such as abrupt changes in intensity. An example of this is shown in figs. 13 and 13A, where several of the lines broaden abruptly at points which are all in the same vertical line, showing that the particles where the broadening commences have all the same kinetic energy. This indicates that at certain places in the discharge tube there is an abnormally large production of the particles corresponding to these parabolas. It will be noticed, however, that it is only some of the parabolas which show this effect, there are others which

are of approximately the same intensity throughout. The measurement of the parabolas shows that the uniform ones correspond to atoms while those with the swellings correspond to molecules. Thus we may at certain places in the dark space have great changes in the production of charged molecules without any change in the production of charged atoms. This proves, I think, that the two are produced by different agencies.

Another argument in favour of this view is the great variation that occurs in the relative intensities of the lines due to the atoms and molecules of the same element when the conditions of discharge are slightly altered. I will confine myself to the case of the lines due to the atoms and molecules of hydrogen. By altering the position of the cathode in the neck of the discharge tube we can make the line due to the atom either more or less intense than that due to the molecule. Thus if the cathode is well inside the neck the line due to the atom is more intense than that due to the molecule, while if the cathode is pushed forward into the bulb the line due to the molecule is more intense than that due to the atom. Examples of this difference are shown in figs. 14 and 15. These changes in the position of the cathode involve changes in the pressure of the gas, for to get the positive rays well developed the pressure has to be higher when the cathode is in the neck than when it protrudes into the bulb, so that it would seem that reduction of pressure favours the formation of charged molecules more than that of charged atoms.

In the discharge tube we have cathode rays, positively electrified atoms and molecules, and rays analogous to soft Röntgen rays; all these are known to ionise a gas when they pass through it. As far as my observations have gone the properties of the positive rays indicate that the cathode particles produce the positively charged molecules, while the moving positively electrified particles produce the positively electrified atoms. I do not mean by this that under no circumstances can a cathode particle produce a positively charged atom, for it would probably do so if it struck one of the structural corpuscles, *i.e.* one of those which bind the two atoms in the molecule together. The number of molecules struck in this way would, however, be only a small fraction of those struck by the rays, so that if this were the only source of ionisation the number of charged atoms would be small compared with that of charged molecules. This, however, is not the case, so that we conclude that moving positively charged atoms and molecules are in the main responsible for the dissociation which produces the positively charged atoms occurring in the positive rays.

I will now pass on to the consideration of another very interesting type of positive ray—the multiply charged atom. I say atom advisedly, because

it is doubtful whether we get among the positive rays multiply charged molecules. The indication of a multiple charge is that the line corresponding to the singly charged carrier is prolonged abnormally towards the vertical. The only case of a line due to a molecule for which I have observed a suspicion of such a prolongation is that of the line for which $m/e = 28$, corresponding to a molecule of nitrogen or carbon monoxide. There is reason for doubting whether this is a genuine prolongation of the molecular line, as, since m/e for aluminium $= 27{\cdot}3$, if any aluminium atoms from the cathode got into the discharge tube, the prolongation might be that of the atomic line of aluminium rather than that of the line due to the molecule of nitrogen.

The rarity of the doubly charged molecule seems to indicate that the shock which produces the double charge is sufficiently intense to dissociate the molecule into its atoms. The uniformity of the intensity of the parabolas corresponding to the multiply charged atoms shows that they acquire this charge at one operation and not by repeated ionisation on their way to the cathode.

The occurrence of the multiple charge does not seem to be connected with the valency or other chemical property of the atom. Of all the elements whose lines I have studied, hydrogen and X_3 (see p. 14) are the only ones which have never appeared with a double charge. Elements as different in their chemical properties as carbon, nitrogen, oxygen, chlorine, helium, neon, a new gas whose atomic weight is 22, argon, crypton, mercury, all give multiply charged atoms. The fact that these multiple charges so frequently occur on atoms of the inert gases proves, I think, that they are not produced by any process of chemical combination.

All the results point to the conclusion that the occurrence and magnitude of the multiple charge is connected with the mass of the atom rather than with its valency or chemical properties. We find, for example, that the atom of mercury, the heaviest atom I have tested, can have as many as 8 charges, crypton can have as many as 5, argon 3, neon 2, and so on. There is evidence that when these multiple charges occur the process of ionisation is generally such that the atom starts either with one charge or with the maximum number, that in the ionisation of mercury vapour, for example, the mercury atom begins either with 1 charge or with 8, and that the particles which produce the parabola corresponding to 5 charges, for example, started with 8 and lost 3 of them on its way through the tube in the cathode. The intensity of the lines corresponding to multiply charged atoms varies greatly with what are apparently but small alterations in the condition of the discharge, a slight alteration in the pressure or in the

position of the cathode may make all the difference between the lines being quite strong or so faint as to be hardly visible.

We shall now pass on to consider the negatively electrified particles which are found mixed with the positive rays. These have much the same energy as the positively electrified ones; they are, in fact, positively electrified until they reach the cathode, they get neutralised after passing through it, and attract another corpuscle, thus getting negatively electrified before reaching the electric and magnetic fields. As they are moving past the corpuscles at a very high speed, in some cases as fast as 2×10^8 cm./sec., it is evident that their attraction for the corpuscles must be very considerable, otherwise they could not grip and hold fast a corpuscle under such conditions. The power of a particle to get negatively electrified may thus be taken as an indication of the strength of the electric field round it, if the electric field is small, *i.e.* if the chemical affinities of the particle are saturated, it will not be able to pick up a corpuscle and become negatively electrified, while it may be able to do so if it is unsaturated and the electric field around it intense.

Now I have not yet found a case where a molecule of a compound gas acquires a negative charge, and only two cases, which will be considered later on, where a molecule of an elementary gas does so. Again, there are some elements whose atoms, when in the positive rays, never acquire a negative charge, such as nitrogen, helium, neon, argon, crypton, and mercury vapour, while negative charges are found on the atoms of hydrogen, carbon, oxygen, sulphur, chlorine. In oxygen the parabolas due to the negatively charged atoms are exceptionally strong; an example of this is shown in the photograph reproduced in fig. 11, which was taken when the gas in the discharge tube was very pure oxygen. Another photograph, showing the lines due to negatively electrified oxygen and carbon atoms, is reproduced in fig. 16.

The two cases where I have found a molecule of an element to be negatively charged are oxygen and carbon. The negatively electrified molecule of oxygen does sometimes occur, although it is by no means common; the conditions for its appearance have not been worked out with certainty, it is probably connected with the presence in the discharge tube of some oxygen compounds of a special type; the negatively charged oxygen atom, on the other hand, occurs in nearly every case when oxygen is present in the tube. It is not perhaps inconsistent with the chemical properties of oxygen to suppose that in some compounds we may have two oxygen atoms united together so as to form a system with a good deal of residual affinity, hydrogen peroxide is perhaps an example of this.

The conditions which regulate the appearance of the negatively charged carbon molecule have been worked out and are very interesting. The negative molecule does not occur in compounds like marsh-gas, carbon dioxide, carbon monoxide, phosgene, and so on, where there is no linking between carbon atoms. On the other hand, it does occur with compounds like acetylene, ethylene, ethane, where there are two carbon atoms linked together by one or more bonds. This is interesting from the chemical point of view because it shows that in such compounds two carbon atoms are held so firmly together that they remain united when the molecule is broken up by the rough treatment it receives in the discharge tube; and secondly, that the system consisting of the two carbon atoms is a highly unsaturated one, as there is an electric field round it strong enough to catch and hold a corpuscle moving past it at a very high speed. In benzene vapour we get negatively electrified triplets of carbon atoms, and I have sometimes thought that I could detect the negative quartet.

The Use of Positive Rays as a Method of Chemical Analysis.

Since each parabola on the photograph indicates the presence in the discharge tube of particles having a known value of m/e, and as by the methods described above we can determine what multiple e is of the unit charge, we can, by measuring the parabolas, determine the masses of all the particles in the tube, and thus identify the contents of the tube as far as this can be done by a knowledge of the atomic and molecular weights of all its constituents. The photograph of the positive rays thus gives a catalogue of the atomic and molecular weights of the elements and compounds in the tube. This method has several advantages in comparison with that of spectrum analysis, especially for the detection of new substances; for, with this method, when we find a new line we know at once the atomic or molecular weight of the particle which produced it. Spectrum analysis would be much easier and more efficient if from the wave-length of a line in the spectrum we could deduce the atomic weight of the element which produced it, and this virtually is what we can do with the positive-ray method.

Again, in a mixture the presence of one gas is apt to swamp the spectrum of another, necessitating, in many cases, considerable purification of the gas before it can be analysed by the spectroscope. This is not the case to anything like the same extent with the positive rays; with these the presence of other gases is a matter of comparatively little importance.

With regard to the sensitiveness of the positive ray method, I have made, as yet, no attempt to design tubes which would give the maximum sensitiveness, but with the tubes actually in use there is no difficulty in detecting the

helium contained in a cubic centimetre of air, even though it is mixed with other gases, and I have not the slightest doubt a very much greater degree of sensitiveness could be obtained without much difficulty.

I will illustrate the use of the method by some applications. The first of these is to the detection of rare gases in the atmosphere. Sir James Dewar kindly supplied me with some gases obtained from the residues of liquid air; the first sample had been treated so as to contain the heavier constituents. The positive-ray photograph reproduced in fig. 17 gave the lines of xenon, crypton, argon, and a faint line due to neon; there were no lines on the photograph unaccounted for, and so we may conclude that there are no heavy unknown gases in the atmosphere occurring in quantities comparable with that of xenon. The second sample from Sir James Dewar contained the lighter gases; the photograph (fig. 18) shows that, in addition to helium and neon, there is another gas with an atomic weight about 22. This gas has been found in every specimen of neon which has been examined, including a very carefully purified sample prepared by Mr. E. W. Watson and a specimen very kindly supplied by M. Claud, of Paris; the photograph of this specimen, fig. 19 (Plate 3), is remarkable, as it shows, in addition to this line and the helium line, a line corresponding to a substance with atomic weight 3, whose properties are discussed later on. The substance giving the line 22 also occurs with a double charge, giving a line for which $m/e = 11$. There can, therefore, I think, be little doubt that what has been called neon is not a simple gas but a mixture of two gases, one of which has an atomic weight about 20 and the other about 22. The parabola due to the heavier gas is always much fainter than that due to the lighter, so that probably the heavier gas forms only a small percentage of the mixture.

Another application of the method was to the analysis of the gas in a small glass tube in which 30 mgrm. of radium bromide had been sealed for more than 10 years. The photograph showed that, in addition to helium, the tube contained considerable quantities of neon, or some gas with about the same atomic weight, some gas of the atomic weight 3 mentioned before, and also a trace of argon, a little more than I should have expected from the volume of air in the tube, although the difference was not very great. The photograph is shown in fig. 20.

The last application of the method I shall bring before you is to the investigation of the gas for which $m/e = 3$. The most convenient way of producing this gas is by bombarding solids by cathode rays. The arrangement used for this purpose is shown in fig. 21. A is a vessel communicating by a tube with the bulb B, in which the positive rays are produced; a tap is placed in the tube, so that the communication between the vessels can be cut

off if desired. A is provided with a curved cathode, like those used for Röntgen-ray focus tubes, and the cathode rays focus on the platform on which the substance to be bombarded is placed. After the solid to be examined has been placed on the platform, the tap between A and B is turned so as to cut

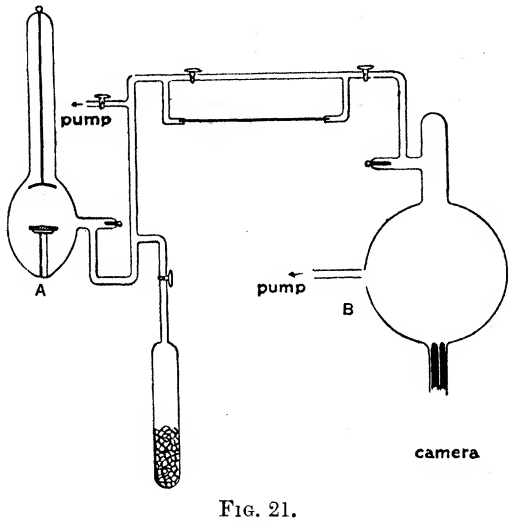

FIG. 21.

off the connection between them, A is exhausted until the pressure is low enough for the cathode rays to be produced, the electric discharge is sent through A, and the cathode rays bombard the solid; the result of this is that in a very short time so much gas, mainly CO_2 and hydrogen, is driven out of the solid that the pressure gets too high for the cathode rays to be formed; to reduce the pressure a tube containing charcoal cooled by liquid air is connected with A, and the gases given off at the commencement of the bombardment are absorbed by the charcoal; after the first rush of gas has come off, the charcoal is cut off from A by the tap.

To analyse the gases given off from the solid, a photograph is taken before the connection between A and B has been opened; after this is finished and when the bombardment has been going on for some hours, the tap is turned and a little of the gas from A is allowed to go into B: another photograph is taken, and the lines in the second photograph which are not in the first represent the gases which have been liberated by the bombardment. The solids tested include platinum, lead (both old and some chemically pure, procured from Kahlbaum), gold, silver, copper, iron, nickel, nickel oxide, zinc, aluminium, magnesium, uranium, palladium, graphite, calcium carbide, diamond dust, mica, lithium chloride, potash, potassium iodide, potassium chloride, fluorspar, two specimens of meteorites, monazite sand, volcanic dust. In every case,

except the two last, a gas whose atomic weight is 3 was found to have been liberated by the bombardment with cathode rays; in some cases the parabola corresponding to it was very well marked, as in the photograph reproduced in fig. 22, which is taken with the gas driven out of platinum (the X_3 line is the third from the top); of the substances tried, the line corresponding to the gas with atomic weight 3, which I shall denote henceforth by X_3, was strongest with platinum, lithium chloride, and potash. The gas continues to come off, even though the bombardment is prolonged for some hours, but in all the cases I have tried it ceases if the bombardment is prolonged for the working hours of several days, and the metal arrives at a state when it can be bombarded without liberating the X_3. The metal before bombardment can be heated to a high temperature without producing much diminution in the supply of this gas given off under the cathode rays, but by heating copper gauze, made of very fine wire, in a vacuum in a quartz tube to a red heat for about 40 hours it was reduced to a state when it no longer gave off X_3 under bombardment.

Helium and in some cases neon or a gas with approximately the same atomic weight are given off along with the X_3 when solids are bombarded by cathode rays. Almost every substance I have bombarded gives off sufficient helium to be detected by this method. After long bombardment, however, the supply of helium gives out, generally long before the X_3 is exhausted. This is hardly to be wondered at, for in most cases the amount of X_3 is much greater than that of helium. In minerals like thorianite, monazite, the two meteorites I examined, and a specimen of volcanic dust, the helium is in excess, in monazite and thorianite the X_3 is but a small fraction of the helium. This method is a very convenient one for analysing the gases in minerals. I may say in passing that helium in small quantities is by no means an infrequent impurity in gases. I have detected it as well as X_3 in some oxygen obtained from a cylinder. I do not mean, however, to imply that all such oxygen contains helium.

With regard to the origin of the gases given out on bombardment, the fact that the emission of gas ceases after prolonged bombardment, and that thin copper wire by long continued heating can be brought to a state in which it ceases to emit the gas, favours the conclusion that in such cases the gas is originally present in the solid, or at any rate is not manufactured *de novo* by the action of the cathode rays alone. The question arises, Are the gases merely absorbed by the solid in the same way that air is absorbed by water or are they constituents of atoms or molecules which are decomposed by the cathode rays? The gas is certainly held with surprising firmness by the metal, the only case in which I have been able to get rid of it by heating is that of

the fine copper wire heated to redness for a week. I have heated lead in a vacuum until two-thirds of it were boiled away and yet the remainder still gave off some helium and X_3 when bombarded by the cathode rays. I tested the gases given out from the lead when heated and found traces of X_3 and also of helium; the quantities obtained in this way were, however, very small compared with those produced by bombardment with cathode rays.

If the gases were absorbed in the solids we should expect to be able to eliminate them by dissolving the solid in water or acid and evaporating the solution to dryness; in some cases, however, this treatment does not reduce the quantity of gas liberated by the cathode rays. A conspicuous instance is lithium chloride: a sample of this when bombarded gave off X_3 and helium, it was then dissolved in water and the solution evaporated to dryness, the freshly deposited lithium chloride gave off X_3 and helium as freely as it did before solution, indeed the helium line seemed to be stronger than before. This process was repeated nine times without leading to any diminution in the gases given out. Similar results are obtained when the LiCl is dissolved in alcohol instead of water and when KHO is substituted for LiCl. It would seem very improbable that any gas merely absorbed or imprisoned by the solid would have been able to withstand this treatment, which, however, would not have eliminated any soluble compound of these gases. This persistence after solution suggests that the gas is in a state of chemical combination and is not merely absorbed in the usual meaning of the term. We shall see that the gas X_3 has some power of entering into chemical combination so that the existence of it as a compound is not impossible. The lithium chloride, however, gives off helium after solution, as well as X_3, so that, assuming that the solution and subsequent heating would eliminate any helium in the free state, the helium must either be generated from LiCl by the bombardment of the cathode rays, or else it must exist in some compound sufficiently stable to admit of being dissolved without decomposition.

In some cases, though not as we have seen in all, solution has the effect of putting the metal into a state in which it does not give off either X_3 or helium when bombarded. Thus I could get no gas from lead freshly deposited as a "lead tree"; again, iron which gave off gas when bombarded ceased to do so when dissolved and re-precipitated. Again, platinum dissolved up in acid and converted into spongy platinum five times in succession, though it did not altogether cease to give off gas under bombardment, did not emit anything like so much as it did before bombardment. The differences in the effects produced by the solution of the metal in different cases would be readily intelligible if these gases formed compounds of different qualities with the different metals.

Though the largest quantities of X_3 are obtained by bombardment with cathode rays, this is by no means the only source of the gas. It and helium are obtained when the discharge from a Wehnelt cathode passes through an exhausted tube. Indeed I had observed the line corresponding to it on several occasions on the photographic plate long before I tried bombarding the solids; its appearance was, however, very sporadic and although I tested a great variety of gases I was never able to get it at will until after a tedious search I hit upon the method of bombarding solids.

I will now pass on to describe the experiments I have made to test the nature of the substance X_3.

The most obvious suggestion is that it is a carbon atom with four charges of electricity. This, however, is not tenable, for the following reasons. The first are based on physical principles. We have seen that a multiply charged atom involves a prolongation of the line due to the singly charged one; in the case of an atom with four charges the primary line would be prolonged until it reached up to one-quarter of the normal distance from the vertical. Now I have never observed a prolongation of the line due to the carbon atom beyond the half distance, this corresponds to a doubly charged atom, and the line for this atom is frequently found on the plate, though always fainter than the primary line. Again, on many of the plates where the X_3 line is strongest there is no prolongation of the line due to the carbon atom at all, and no line corresponding to the doubly charged atom. In some cases, indeed, the X_3 line is stronger than the primary carbon line, and in all cases when the gas is generated by bombardment stronger than the doubly charged carbon line. This is the argument from the physical side; there is, however, another argument based on consideration of a chemical character. The gas X_3 can be stored and tested weeks after the bombardment has taken place. If then the line is due to the carbon atom with four charges it must be that some carbon compound is produced by the bombardment which, when introduced into the discharge tube, gives a plentiful supply of carbon atoms with four charges. Now I have put directly into the tube all the gaseous carbon compounds I could get, including marsh-gas, carbon dioxide, carbon monoxide, carbon tetrachloride, phosgene gas, carbon bisulphide, cyanogen, acetylene, ethylene, ethane, the vapours of a number of alcohols and ether, benzene, coal gas, without getting a trace of the X_3 line. Again, X_3 can resist treatment with hot copper oxide and potash, which would remove the carbon compounds. For these reasons we may, I think, put aside the idea that X_3 is due to carbon.

If X_3 does not contain a new element and is not carbon with four charges

it must be triatomic hydrogen. From the physical side there is considerable evidence in favour of this view; for example, whenever X_3 is freely produced by bombardment, it is always accompanied by large quantities of hydrogen: we may, however, have large quantities of hydrogen without X_3. The chemical properties of X_3, however, in no way suggest hydrogen, so that if it is manufactured from that gas its relations to hydrogen must be very different from those of ozone to oxygen. The properties of X_3 brought to light by these experiments are as follows:—

It can be kept over mercury for several weeks, although it is diminished in amount at the end of that time.

It can be heated in a quartz tube for several hours without any appreciable change, although the quartz is at a red heat.

It can be sparked with oxygen and also with phosphorus without being destroyed.

It is not affected when passed over cold metallic sodium, and when heated with sodium vapour it does not combine with it.

It can withstand the action of red-hot copper oxide and potash. This experiment was tried seven times, in two cases there was an appreciable diminution in the quantity of X_3, in the others there was no effect. The exceptional cases, I am inclined to think, were due to some of the copper being reduced, as hot copper combines, to some extent, with X_3. Fig. 23 (3) is from a photograph when the gas had passed over hot copper oxide; 23 (2) and (4) of the same gas which had not been treated. 23 (1) is the check taken before the gas was admitted; it does not show the 3′ line or the helium, which would come just under the strong line at the top, which is due to the hydrogen molecule.

It can stand over potash for several days without being absorbed

These properties point to its being a very inert substance, and are not those we should expect an allotropic form of hydrogen to possess. I have found, however, two cases where it enters into chemical combination—

(1) It combines with mercury vapour when an electric discharge is sent through the mixture.

(2) It combines, to some extent, with red-hot copper. This is illustrated by the photograph reproduced in fig. 24; (1) is the check before introducing the gas, (2) and (4) that of gas not passed over copper; (3) that of the gas after passing the copper, in this the 3′ line is fainter than in (2) and (4).

These properties point to the conclusion that if X_3 is an element it has considerable resemblance to the inert gases helium and argon, although its chemical properties are slightly more energetic. The absence of parabolas corresponding to $m/e = 1{\cdot}5$ and $m/e = 6$ shows that if it is an element it

is monatomic. Mendeléeff predicted the existence of an element of atomic weight 3, and attributed to it properties similar to those of fluorine, but of greater intensity. The chemical properties of X_3 are much too lethargic to be consistent with the view that it is a kind of super-fluorine. If X_3 is related to such an element, that element must have an atomic weight 2 and not 3, and X_3 must be a stable compound of it with hydrogen. If this were the case, since the line corresponding to the element would coincide with that due to the hydrogen molecule, which is always on the plate, it would be difficult to get, by the study of the lines due to the positively charged particles, evidence as to its existence. We should expect, however, that a substance possessing the energetic chemical properties of Mendeléeff's element would be able to attract a negative charge, and that there would be on the negative side of the photographs a line for which $m/e = 2$. I have not, however, as yet been able to detect the existence of such a line. Again, with but three exceptions, H, B, N, all the atomic weights less than 40 are of the form $4n$ or $4n+3$; if the atomic weight of X_3 were 2 it would be another exception to this law.

I have much pleasure in thanking Mr. F. W. Aston, B.A., of Trinity College, and Mr. E. Everett, for the invaluable assistance they have given me with these experiments.

[*Note added June* 14, 1913.—In the experiments described in the lecture the evolution of X_3 and helium from metals under bombardment by cathode rays was in most cases much smaller when the metals had been freshly deposited, and the solution evaporated to dryness, than it was with metals which had not been so treated. The supply of helium, too, soon gave out under bombardment, indicating that the helium had been absorbed by the metal and was liberated by the bombardment. There was one case, however, that of LiCl, in which solution produced no diminution in the amount of helium given out. This result led me to examine within the last few days the effect of bombarding by cathode rays the salts of the alkali metals and of the alkaline earths; these experiments have convinced me that when the salts of Li, Na, K or Rb are bombarded by cathode rays there is a genuine production, as distinct from liberation of absorbed gas, of helium and X_3, potassium giving the largest supply. The amount of helium obtained from these elements was much larger than that from any of the substances I have tried other than minerals such as monazite sand, thorianite, volcanic ash, or meteorites, which are known to contain free helium. On the other hand, the salts of calcium, ammonium, and silver, have shown no special power of

giving out helium; the very small amount obtained was not more than could be accounted for by absorbed gas, they produce X_3, however, quite freely.

The advantage of using the salts instead of the metals themselves is that, by solution in water or alcohol and subsequent evaporation to dryness, they can be freed from absorbed helium and X_3. The salts examined were LiCl, LiOH, Li_2CO_3, NaCl, KHO, KI, KCl, RbI, NH_4Cl, $CaCl_2$, CaO (this was a portion of a lime-light cylinder), and AgCl. The lithium, sodium, potassium, and rubidium salts showed the helium line strongly, especially the potassium salts; indeed, except with minerals which are known to contain helium, I have never seen the helium line so strong as it was when KI was bombarded. The strength of the He line was not diminished by repeated solution and evaporation; on the contrary, it was increased sometimes to a considerable extent. I think this increase may be a secondary effect, due to the elimination from the salt of the ordinary absorbed gases, such as H_2 and CO_2. The result of this is that a smaller amount of gas comes off when the salt is bombarded, the pressure in the bombardment chamber is lower, and the cathode rays are faster and more energetic. The helium did not come from the electrodes, for when CaO or AgCl was bombarded with the same electrodes, at the same pressure and for the same time, little or no helium was produced. As an additional precaution, the cathode was scraped from time to time. All the samples of the salts I have tried give the same results. This makes it improbable that the effects are due to the presence of some helium-containing mineral like monazite sand. I have dissolved some of the salts in alcohol, and filtered the solution, without diminishing the supply of helium; thus any helium-containing impurity must be soluble in alcohol.

On the plate on which the helium line was strongest—the salt was KI—I could see a very faint line corresponding to an atomic weight 35 or thereabouts. I should have thought this was due to a trace of chloride among the potassium iodide, except for the fact that when KCl was substituted for KI this line was not strengthened. I have not yet been able to get this line strong enough to measure it with sufficient accuracy to decide whether the particle producing it has an atomic weight exactly equal to the difference of the atomic weights of potassium and helium.

The evolution of helium in exceptionally large amounts from the alkaline metals is interesting, since potassium, as Mr. Campbell has shown, is radioactive. I am disposed to regard the emission of helium from these metals as supporting the speculation I gave in a letter to 'Nature,' Feb. 13, 1913, that other elements besides radium, thorium, and the like, make attempts to expel α-particles (atoms of helium). In ordinary elements these particles have not enough energy to get away from the atom; they are, however, as

it were, loosened, and can be detached by vigorous bombardment with cathode rays.

I now pass on to consider the effect of solution and subsequent evaporation on the evolution of X_3, which all the salts, including the calcium, ammonium, and silver ones, gave off in abundance. Solution and evaporation produced a marked diminution in the output of X_3 from Li_2CO_3, KI, KCl. It had little effect, however, on the output from LiCl, LiOH, KOH, $CaCl_2$. It will be noticed that these latter salts are very deliquescent, while those which are affected by solution are not. This suggests that the diminution in X_3, when it occurs, may be due to water being driven off when the salts are strongly heated after evaporation, the deliquescent salts recovering the water before bombardment, whilst the others do not. The X_3 will come out of the salt with cathode rays which are not fast enough to liberate helium.

These results show, I think, that the X_3 liberated from the dissolved salts was not simply absorbed by them, but was either manufactured from hydrogen in the presence of water, or liberated from the atoms of one or more of the elements in the salt, and that the presence of water is an important, it may be an essential, condition for its production by atomic disruption. If we suppose X_3 is made from hydrogen the function of the salt may be merely to supply the necessary water in a convenient form. X_3 is produced when the discharge from a Wehnelt cathode passes through gas at a low pressure, though in this case the bombardment of the walls of the tube by cathode rays is feeble; this and its sporadic appearance in discharge tubes would be accounted for if it were produced from water vapour.]

[*Note added July* 10, 1913.—I find that X_3 disappears when a mixture of it with hydrogen is sparked with sufficient oxygen to give a violent explosion.]

FIG. 2.

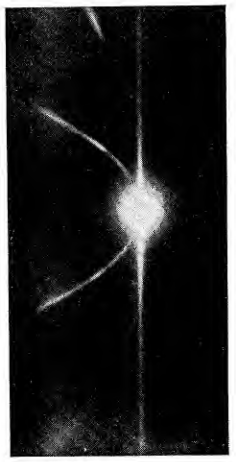

FIG. 3.

FIG. 7.

FIG. 10.

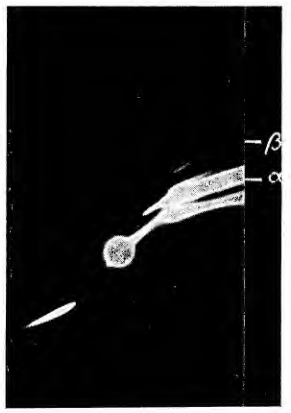

FIG. 11.

FIG. 13.

FIG. 13A.

FIG. 14.

FIG. 15.

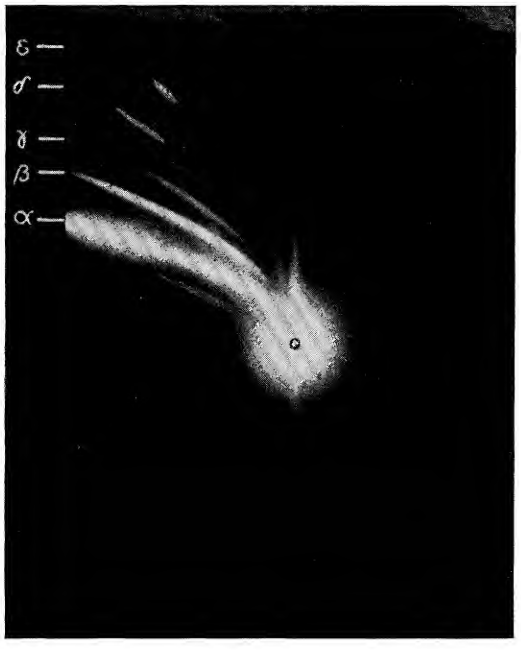

FIG. 12.

FIG. 16.

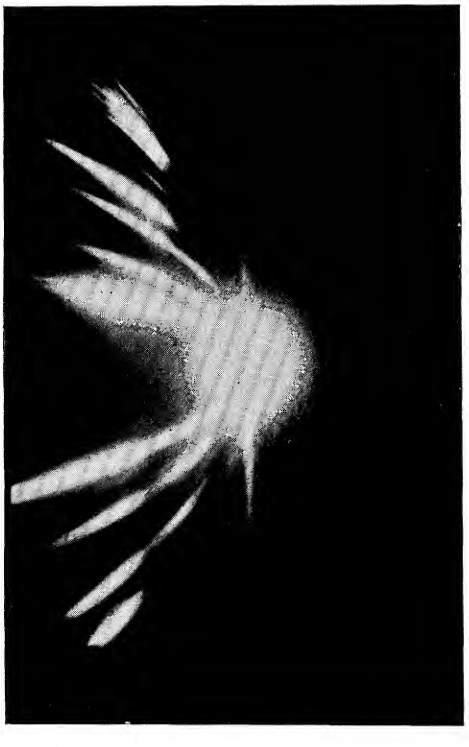

FIG. 17.

FIG. 18.

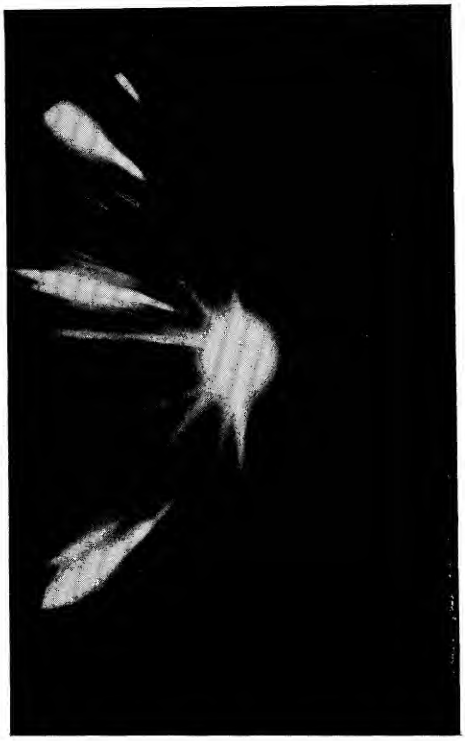

FIG. 19.

FIG. 20.

FIG. 22.

FIG. 23.

FIG. 24.

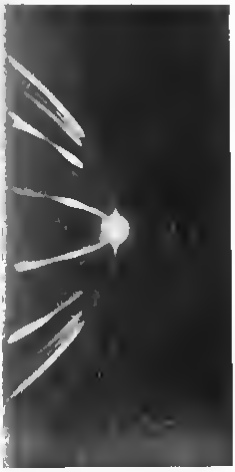

FIG. 2.

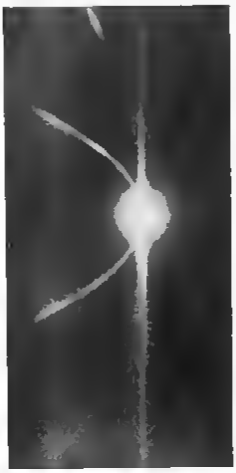

FIG. 3.

FIG. 7.

FIG. 10.

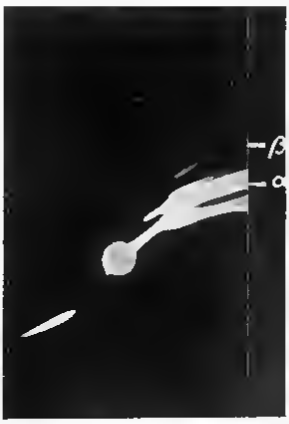

FIG. 11.

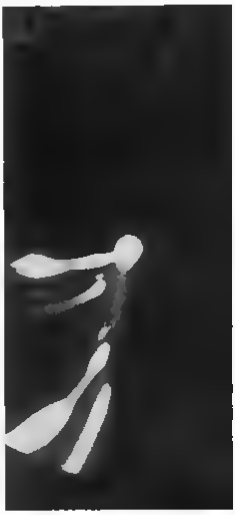

FIG. 13.

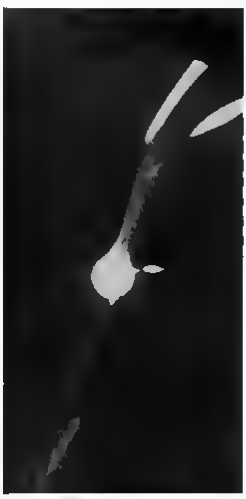

FIG. 13A.

FIG. 14.

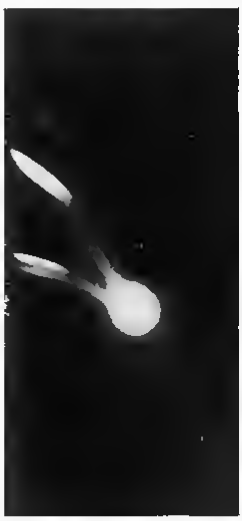

FIG. 15.

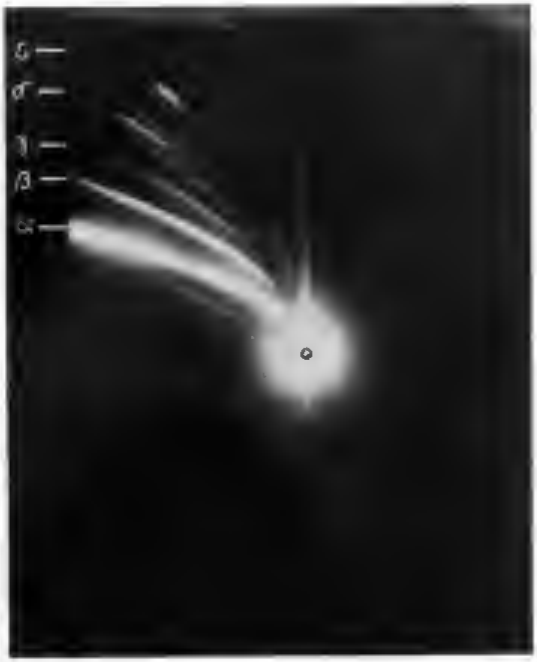

FIG. 12.

FIG. 16.

FIG. 17.

FIG. 18.

FIG. 19.

FIG. 20.

FIG. 22.

FIG. 23.

FIG. 24.